Diffusion in a Medium with a Random Distribution of Static Traps

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(Received 18 April 1983)

Particles diffusing in d-dimensional space among a random distribution of stationary spherical traps are considered. Given a particle at the origin at time $t=0$, it is shown that the density of particles at the origin as $t\to\infty$ must decay at least as fast as $\exp[-t^{d/(d+2)}]$. The density here is obtained by averaging the diffusive field for a given configuration of traps over all configurations. The present upper bound coincides with the lower bound recently derived by Grassberger and Procaccia.

PACS numbers: 05.60.+w, 66.10.Cb, 82.20.Db

Numerous authors have recently considered both steady state and transient situations in which particles diffuse through a medium with a random distribution of stationary traps (reaction sites, sinks).[1-11] The main objective has been to express the reaction rate constant, the effective diffusion coefficient, and the particle number density at long times as expansions in the trap density. We show in this Letter that such expansions cannot be used to study the long-time transient behavior.

The problem we consider is the following. With Λ a particular realization of the random distribution of traps, let $\rho_\Lambda(\vec{r},t)$ denote the number density of diffusing particles at position $\vec{r}$ and time t. The traps are taken to be spheres of radius $a>0$ distributed with average number density n_s according to a uniform probability distribution. Their positions are therefore totally uncorrelated and they are allowed to overlap. The density $\rho_\Lambda(\vec{r},t)$ satisfies the diffusion equation

$$\partial_t \rho_\Lambda(\vec{r},t)=D\nabla^2\rho_\Lambda(\vec{r},t),$$

with the boundary condition $\rho_\Lambda(\vec{r},t)=0$ on the surface of each trap, where D is the diffusion coefficient of the particles in the absence of traps. The trap-averaged density is then defined as $\rho(\vec{r},t)=\langle\rho_\Lambda(\vec{r},t)\rangle_\Lambda$. Given the initial condition $\rho_\Lambda(\vec{r},0)=\delta(\vec{r})$, our goal is to derive an upper bound on $\rho(\vec{0},t)$ at long times.

Our result may be stated as follows:

$$a^d\rho(\vec{0},t)<\exp[-A(n_s^{2/d}Dt)^{d/(d+2)}], \qquad (1)$$

where $d=2,3,\ldots$ is the dimensionality of space and A is a dimensionless constant. The time exponent $d/(d+2)$ is interpreted in the same sense as an exponent in the theory of critical phenomena,[12] and so the result could be modified by factors of $\ln t$ (which has exponent zero). Our derivation in fact leads to $d/(d+2)-\epsilon$, where ϵ is arbitrarily small. The upper bound (1) has the same form as the lower bound recently derived by Grassberger and Procaccia (GP),[10] and so the asymptotic time exponent $d/(d+2)$ may now be regarded as exact.

The GP lower bound shows that the behavior of $\rho(\vec{r},t)$ at long times cannot be obtained from a conventional reaction-diffusion equation

$$\partial_t\rho(\vec{r},t)=D\nabla^2\rho(\vec{r},t)-k\rho(\vec{r},t), \qquad (2)$$

where k is a rate constant. Our result, on the other hand, unequivocally rules out the possibility of long-time tails (algebraic decay), such as are implied by approaches based on expansions about $n_s=0$.[4,13] It is apparent from (1) that expansions in the trap density diverge exponentially at long times, so that traditional perturbative techniques cannot be employed.

Before presenting the details of the derivation, we briefly sketch its physical basis. The reaction-diffusion equation is usually obtained by first averaging over the positions of the traps, so that one obtains a uniform partially absorbing medium characterized by a rate constant k. Equation (2) then predicts an exponential decay of ρ at long times, $\rho(\vec{r},t)\sim\exp(-kt)$. The GP lower bound shows that this is incorrect and one must first calculate the density for a given configuration of traps before averaging over the positions of the traps. The preaveraging procedure fails because almost every trap configuration contains arbitrarily large "holes," i.e., regions completely free of traps. While the probability of finding a diffusing particle in such a hole is quite small, the associated density field decays very slowly. It is the competition between these two factors which in fact gives rise to the GP lower bound. Our approach is based on a procedure whereby we classify trap configurations according to whether a large volume centered at the origin contains large holes. We thus isolate such configurations and those that remain are in some sense spatial-

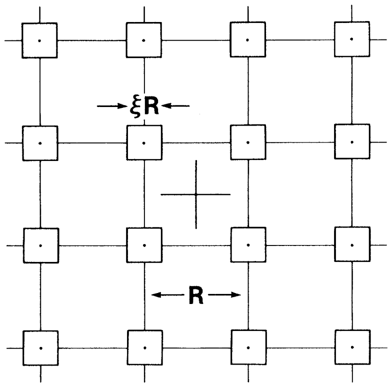

FIG. 1. The system of cubes of edge ξR used to classify trap configurations. The origin is located at the center of the system.

ly uniform. These are then amenable to treatment by a reaction-diffusion equation.

To perform the classification of trap configurations, we introduce the mathematical network of cubes of edge ξR depicted in Fig. 1. These lie on a cubic lattice with lattice spacing R and finite extent NR. We assume that $\xi \ll 1$, $\xi R \gg a$, $N \gg 1$, and $n_s(\xi R)^d \gg 1$. The last inequality implies that the expected number of traps in any of the cubes of edge ξR is extremely large. We take ξ to be some small fixed number throughout, while later we adjust R and N to optimize the derived upper bound.

The trap-averaged density at the origin, $\rho(\vec{0},t)$, may be written

$$\rho(\vec{0},t)=\sum_{\Lambda}\rho_{\Lambda}(\vec{0},t)p_{\Lambda},$$

where p_Λ is the probability of a given realization of traps, Λ. We now express $\rho(\vec{0},t)$ as the sum of two terms: one involving those realizations Λ_1 for which at least M cells of edge ξR are empty, and the other involving those realizations Λ_2 for which fewer than M cells of edge ξR are empty. Thus,

$$\rho(\vec{0},t)=\sum_{\Lambda_1}\rho_{\Lambda_1}(\vec{0},t)p_{\Lambda_1}+\sum_{\Lambda_2}\rho_{\Lambda_2}(\vec{0},t)p_{\Lambda_2} \tag{3}$$

and we bound these two contributions separately.

In the first sum, $\rho_{\Lambda_1}(\vec{0},t)$ is smaller than the density one would have if there were no traps present anywhere, and from the solution to the diffusion equation in the absence of traps we can therefore write

$$\rho_{\Lambda_1}(\vec{0},t)<(4\pi Dt)^{-d/2}.$$

Furthermore, $\sum_{\Lambda_1}p_{\Lambda_1}=P_M$ is the probability that at least M cells of edge ξR are empty, and so we have

$$\sum_{\Lambda_1}\rho_{\Lambda_1}(\vec{0},t)p_{\Lambda_1}<(4\pi Dt)^{-d/2}P_M.$$

The probability P_M is easily calculated. Since the probability that a given cell is empty is given by the Poisson result $\exp[-n_s(\xi R)^d]$, we have

$$P_M=\sum_{m=M}^{N^d}\binom{N^d}{m}\exp[-mn_s(\xi R)^d]\{1-\exp[-n_s(\xi R)^d]\}^{N^d-m}.$$

To deduce a simpler upper bound on P_M, we further assume that

$$N^d\exp[-n_s(\xi R)^d]\ll 1, \quad N^d \gg M \gg 1.$$

The first condition makes the summand a decreasing function of m, and using Stirling's formula in the resulting bound we obtain

$$P_M<N^d\exp[-Mn_s(\xi R)^d+M\ln(N^d/M)].$$

Our final upper bound on the first sum in (3) therefore becomes

$$\sum_{\Lambda_1}\rho_{\Lambda_1}(\vec{0},t)p_{\Lambda_1}<(4\pi Dt)^{-d/2}N^d\exp[-Mn_s(\xi R)^d+M\ln(N^d/M)]. \tag{4}$$

With regard to the second term in (3), we observe that $\rho_{\Lambda_2}(\vec{0},t)$ must be smaller than the density obtained by deleting all traps outside the cells of edge ξR, and if a given cell of edge ξR happens to contain traps we delete all but one. The remaining traps thus lie approximately on a cubic lattice with lattice spacing R and finite extent NR, and by construction no more than M of the cells of edge ξR can be empty. We can in fact assume that there are exactly M empty cells, and for obvious reasons we refer to these as vacancies. To obtain an upper bound on $\rho_{\Lambda_2}(\vec{0},t)$ we thus need only estimate the density at the origin for such an arrangement of traps. We first consider the problem of an infinite cubic lattice with a trap located at each lattice site, and we then discuss the following three effects: (1) the finite extent of our lattice, (2) small deviations of traps from lattice sites, and (3) vacancies.

It is possible to derive a rigorous upper bound on the long-time decay of the density at the origin for an infinite cubic lattice of traps,[14] but we will present an intuitive derivation that leads to the same result. To begin with, one would expect $\rho(\vec{0},t)$ to decay exponentially at long times, and this is because a perfect lattice of traps can be considered globally homogeneous on length scales much larger than the lattice spacing R; that is, the density of traps viewed on such scales appears uniform. The key point here is that a lattice of traps does not have arbitrarily large holes that lead to a breakdown of the reaction-diffusion equation. Thus, at long enough times we expect $\rho(\vec{r},t)$ (appropriately coarse grained) to satisfy (2), i.e.,

$$\rho(\vec{0},t)\sim\exp(-kt)$$

for $kt\gg1$. The form of the decay constant k follows almost by dimensional analysis. Since k has the dimensions $(\text{time})^{-1}$, it must depend linearly on the diffusion coefficient D. Moreover, for $R\gg a$ one expects k to be proportional to the number density of traps, R^{-d}. The only other length in the problem is then the trap radius a, and these considerations therefore lead to

$$k=k_0(D/a^2)(a/R)^d,$$

where k_0 is a dimensionless constant. The more mathematical analysis shows that k must in fact be multiplied by a factor of $[\ln(R/a)]^{-1/2}$ in two dimensions, but in view of the scaling introduced below and our earlier statement regarding exponents we omit this factor. Combining the expressions for $\rho(\vec{0},t)$ and k, we therefore have

$$\rho^*(\vec{0},t)=a^{-d}\exp[-k_0a^{d-2}Dt/R^d]. \quad (5)$$

The asterisk indicates that this is the result for an infinite cubic lattice of traps, and the unimportant factor of a^{-d} has been introduced only for dimensional consistency.

We now assess the three effects mentioned above, starting with the finite extent of the lattice. The result (5) is not in fact valid for a finite lattice at arbitrarily large times, but it does hold at times such that

$$k_0a^{d-2}Dt/R^d\gg1, \quad (6)$$

$$Dt/(NR)^2\ll1. \quad (7)$$

The first inequality simply implies that we would be in the exponential regime if the lattice were infinite, while the second implies that at the times considered the diffusing particle has not yet had a chance to diffuse to the boundary of the lattice. In this intermediate-time regime the lattice can therefore be regarded (in a coarse-grained sense) as an effectively infinite, partially absorbing continuum. With regard to small deviations of the traps from lattice sites (recall that $\xi R\ll R$), these can clearly have no effect on the result (5) since an almost-perfect lattice of traps is also globally homogeneous when viewed on a large enough length scale. All that remains is to consider the effect of M vacancies, and the density at the origin should be largest when these lie in a sphere centered at the origin. Assuming that (6) and (7) are satisfied, we then have the rough physical picture of an effectively infinite, partially absorbing medium with a spherical hole of radius $M^{1/d}R$ cut out at the origin. The condition that (5) hold for this problem is that, in addition to (6) and (7), $D/k(M^{1/d}R)^2\gg1$, i.e.,

$$(R/a)^{d-2}/k_0M^{2/d}\gg1. \quad (8)$$

This is the only dimensionless parameter in the problem [given (6) and (7)], and (5) reduces to the correct answer in limiting cases, e.g., $M\to0$. In summary, we conclude that (5) is valid for all Λ_2-type configurations provided (6)–(8) are satisfied.

Returning to the second term in (3), we can write $\rho_{\Lambda_2}(\vec{0},t)<\rho^*(\vec{0},t)$, $\sum_{\Lambda_2}p_{\Lambda_2}<1$, so that

$$\sum_{\Lambda_2}\rho_{\Lambda_2}(\vec{0},t)p_{\Lambda_2}<\rho^*(\vec{0},t),$$

and with this result and (4) and (5), (3) becomes

$$\rho(\vec{0},t)<(4\pi Dt)^{-d/2}N^d\exp[-Mn_s(\xi R)^d+M\ln(N^d/M)]+a^{-d}\exp[-k_0a^{d-2}Dt/R^d]. \quad (9)$$

We now imagine that some arbitrarily large value of the time t is specified, and to obtain the best possible upper bound we adjust the parameters R, N, and M to make the right-hand side decay as fast as possible for $t\to\infty$. For this purpose we set $M=N^{d(1-\gamma)}$ with $0<\gamma<1$, and assume that $R\sim t^\alpha$, $N\sim t^\beta$ with α, $\beta>0$. We thus let R and N grow with the time. In terms of the exponents α, β, and γ, the inequalities (6)–(8) take the form

$$\alpha<1/d,\quad 2\alpha+2\beta>1,\quad (d-2)\alpha-2\beta(1-\gamma)>0,$$

and one may easily verify that the other inequalities introduced thus far are satisfied. Neglecting higher-order terms in the exponents in (9), we can therefore write $\rho < \exp(-t^q)$, where

$$q = \sup\{\min[d\alpha + d\beta(1-\gamma), 1 - d\alpha]\}.$$

The supremum (least upper bound) is with respect to all allowed values of α, β, and γ, and after some algebra we in fact obtain $q = d/(d+2)$. [If we require the conditions on α, β, and γ to be satisfied as strict inequalities, we find $q = d/(d+2) - \epsilon$, where ϵ is arbitrarily small.] The corresponding values of α, β, and γ are $\alpha^* = 2/d(d+2)$, $\beta^*(1-\gamma^*) = (d-2)\alpha^*/2$, $d^2/(d^2+2d-4) \leq \gamma^* < 1$.

To fix the coefficient of $t^{d/(d+2)}$ in the exponent, we set $R = a(k_0/A)^{1/d}(Dt/a^2)^{\alpha^*}$ and $N = \tilde{N}(Dt/a^2)^{\beta^*}$, where $\tilde{N}^{d(1-\gamma^*)} = A^2/k_0\xi^d n_s a^d$ and A is a time-independent dimensionless adjustable parameter. Our final upper bound on $\rho(\vec{0},t)$ then becomes

$$a^d\rho(\vec{0},t) < \exp[-A(Dt/a^2)^{d/(d+2)}]. \quad (10)$$

The choice $A = \text{const} \times (n_s a^d)^{2/(d+2)}$ yields an upper bound of the same form as the lower bound derived by Grassberger and Procaccia and corresponds to the result given as (1). Note that there is no inconsistency between the GP lower bound and our upper bound even when we take A to be arbitrarily large. This is because GP obtain $q = d/(d+2)$ identically, whereas our method yields $q = d/(d+2) - \epsilon$.

In conclusion, our method can also be used to bound the relative fluctuations about $\rho(\vec{0},t)$ (they are large), and can be extended to take into account trap excluded-volume effects. A close connection between the problem considered here and the quantum mechanical Lorentz gas should also be noted.[15,16] The techniques developed there might prove useful in correctly modifying (2). Only a limited amount of progress in that direction has been made.[9]

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